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RING OPENING POLYMERIZATION OF CYCLOTETRASILANES: A VERSATILE ROUTE TO LINEAR POLYSILYLENES.
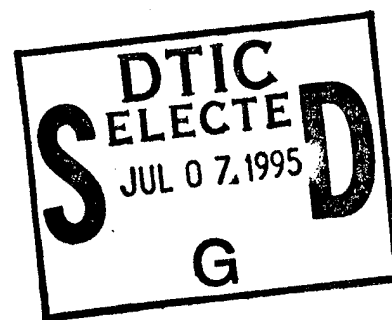
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Abstract. This paper reviews ring opening polymerization (ROP) of cyclotetrasilanes. The ROP of cyclotetrasilanes is an interesting and versatile method to prepare both polysilylenes homo and copolymers which cannot be prepared by other methods. First fundamentals of ROP are discussed with a special emphasis on thermodynamics and kinetics as well as chemoselectivity, regioselectivity, and stereoselectivity. Subsequently, a basis of silicon chemistry, including Si-Si bond formation and cyclosilanes, is covered. A variety of cyclotetrasilanes, $Me_nPh_{8-n}Si_4$, where n = 3, 4, 5, or 6, were prepared and polymerized using silyl cuprates as initiators. The polymerization of the all-trans isomer of $Me_4Ph_4Si_4$ proceeded with two inversions of configuration at both the attacked silicon atom in the ring and the newly formed reactive center resulting in a polymer with 75% heterotactic triads and 25% isotactic triads. Polymerization of the tri-, penta-, and hexamethyl derivatives proceeded with some degree of regioselectivity. Block copolymers were prepared by the subsequent addition of $Me_4Ph_4Si_4$ to either polystyryl lithium or polyisoprenyl lithium. A novel block copolymer of two different polysilylenes was synthesized by the copolymerization of a masked disilene and $Me_4Ph_4Si_4$. Segmental copolymers of poly(ferrocenylsilane) and PMPS were prepared by the thermal copolymerization of $Me_4Ph_4Si_4$ and [1]-silylferrocenophanes.

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1 INTRODUCTION

Polysilylenes (polysilanes) consist of linear chains of silicon atoms bearing two substituents, generally either alkyl or aryl[1-3]. Polysilylenes have unique properties, such as sigma delocalization which gives rise to intense UV absorptions. Thermochromic behavior has also been observed in some systems. Because of these properties the polysilylenes have found potential applications as photoconductors and non-linear optical materials. The electronic properties depend on the substituents, the chain conformation, the solvent, and the temperature[4-7]. For example, in solid poly(di-n-hexylsilylene) the backbone conformation changes abruptly from an all-trans planar zig-zag conformation ($\lambda_{max} \approx 370$ nm) to a columnar mesophase with a less rigid conformation ($\lambda_{max} \approx 315$ nm) upon heating above 42 °C[8]. Because the properties of polysilylenes depend on the conformation of the backbone, which may be affected by the configuration of the substituents, the preparation of polymers with controlled microstructures is of great importance.

Polysilylenes can be prepared by several synthetic methods including: 1) the reductive coupling of dichlorosilanes[1-3], 2) dehydrogenative coupling of primary silanes[9], 3) anionic polymerization of masked disilenes[10], and 4) ring opening polymerization of cyclotetrasilanes[11]. Only the latter two methods lead to well-defined systems.

Ring opening polymerization, ROP, allows for potential control over the resulting microstructure because monomers with known configurations of substituents can be prepared[12]. ROP also allows for control of the molecular weights, molecular weight distributions[13], and enables the preparation of block copolymers[14]. In addition, ROP may be used for the synthesis of polysilylenes possessing substituents which would not survive the reductive coupling conditions. This paper describes the versatility of the ROP method for the synthesis of polysilylenes and polysilylene based materials.

2 FUNDAMENTALS OF ROP

In order to successfully accomplish ROP, several criteria need to be satisfied including both the kinetic and thermodynamic polymerizabilities of monomers, temperature and concentration effects, and selection of the proper active centers during the polymerization process.

2.1 Thermodynamics and Kinetics

As with most polymerization processes, ROP is accompanied by a large decrease in entropy. This is a result of the loss of three degrees of translational freedom for each monomer unit as it is incorporated into the linear chain. The loss in entropy must be compensated for by a release of the ring strain. Therefore, nearly all ROPs are strongly exothermic and most strained three, four, but only some five, six, seven, and larger membered rings can be polymerized. Polymerization can only occur when the overall free energy is reduced, therefore, successfull ROPs takes place below a certain temperature called the ceiling temperature.

$$T_c = \frac{\Delta H_p{}^o}{\Delta S_p{}^o + Rln[M]_o} \tag{1}$$

For weakly strained rings, such as nonamethylphenylcyclopentasilane, the ceiling temperature is extremely important and this monomer can only be polymerized at very low temperatures (-78 °C) and high concentrations[15].

The opposite is seen in some cases, such as in the polymerization of eight membered sulfur and selenium compounds, where the overall entropy is increased during ROP and no ring strain is released. These exceptions possess a floor temperature instead of a ceiling temperature, and elemental sulfur can only be polymerized above $T_f \approx 160$ °C.

According to equation (1), concentration effects are also seen in ROP processes and there exists an equilibrium monomer concentration, $[M]_e$. No polymerization is observed if the initial monomer concentration, $[M]_o$, is less than $[M]_e$. For example, in the room temperature cationic polymerization of tetrahydrofuran, $[M]_e$ is equal to 3 mol/L and in bulk THF $[M]_o$ is equal to 12 mol/L which allows for successful polymerizations to be performed[16]. For more strained 4-membered rings, the equilibrium concentration is quite low ($[M]_e \ll 0.1$ mol/L) and concentration effects become less important. In some cases, strained rings can be converted to strainless macrocycles rather than to linear, high molecular weight polymers. This process can occur either via an end-biting or backbiting mode and depends strongly on the mechanism of polymerization. For example, ethylene oxide can be converted to high polymers in the presence of anionic initiators, but gives predominantyl 1,4-dioxane under cationic conditions. In some cases intramolecular cyclization can be avoided if polymerizations are carried out under the kinetic regime by terminating before backbiting can occur.

2.2 Chemoselectivity, Regioselectivity, and Stereoselectivity

In order to prepare high molecular weight polymers the ratio of the propagation rate constant to the rate constants for side reactions must be quite high (> 100). This ratio defines the chemoselectivity of the system. Possible side reactions may involve reaction of the active species with functionalities present in the monomer resulting in termination and/or transfer. Therefore, the proper choice of active species is imperative. Control of the molecular weight of the prepared polymers is also desired. In some systems the molecular weight can be controlled by varying $[M]_o/[I]_o$. If the propagating centers are selective only to a specific site in the monomer and no termination or transfer reactions are present, then a living system can be achieved. However, to prepare polymers with narrow molecular weight distributions, M_w/M_n, initiation must be as fast as propagation.

In addition to the need for chemoselectivity, more subtle differences in polymerizations include regioselectivity and stereoselectivity. Monomer units may be connected in several fashions leading to head to tail, head to head, or tail to tail structures and the resulting regiochemistry has a large influence on the properties of the polymer. In cyclic monomers which possess chiral or prochiral atoms, there exists the possibility for different stereochemical outcomes as well. Different microstructures often lead to dramatically different physical properties as in the case of polypropylene where

syndiotactic and isotactic polypropylene are highly crystalline, while atactic polypropylene is an amorphous material.

3 SILICON CHEMISTRY

3.1 Silicon Bonds

Si-Si bonds are similar to their group IV counterpart C-C bonds, but differ in bond length (2.3 versus 1.54 Å) and are slightly weaker (280-340 versus 340 kJ/mol). However, Si-Si bonds have considerably different electronic structures than C-C bonds.

Even though there are no π orbitals present, the Si-Si bonds show absorptions at low energy, beginning around 200 nm for disilanes and reaching a maximum of above 300 nm, even up to 400 nm depending on the conformation and substituents, at chain lengths above 100 silicon atoms, while alkanes show no absorptions above 160 nm. These low energy absorptions have been attributed to a σ-σ^* excitation.

While double and triple bonds are very common for carbon systems, very few silicon compounds with double bonds, disilenes, have been prepared and only when the substituents at silicon are very bulky, such as mesityl groups[17,18]. Bond lengths in disilenes are in the range of 2.1 Å. Si=Si containing compounds will spontaneously polymerize unless they are protected by sterically crowded substituents which place the free energy of the hypothetical linear polymer above that of the disilene.

3.2 Si-Si Bond Synthesis

Si-Si bonds can be formed in a variety of different reactions as depicted in Scheme 1. The most widely used method is nucleophilic displacement. This has been employed in

Scheme 1
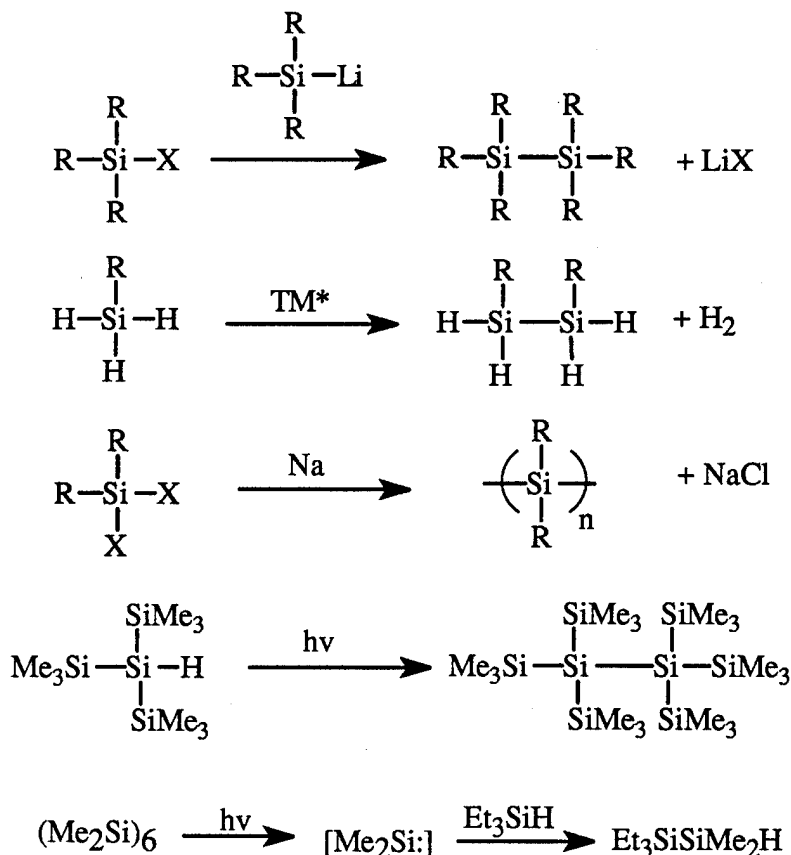
polymer chemistry in both the anionic polymerization of masked disilenes and the ROP of cyclotetrasilanes. A second method for preparing Si-Si bonds is the dehydrogenative coupling of primary silanes using transition metal catalysts. Silicon halides can be coupled by the use of group I metals such as Li, Na, and K. A less selective route is the coupling of silicon radicals formed by the photochemical scission of Si-Si or Si-H bonds. Trapping of silylenes, such as $Me_2Si:$, with Et_3SiH results in the insertion of the silylene and formation of a Si-Si bond. The limited selectivity of the latter two methods prohibits their use in the preparation of high molecular weight polymers.

3.3 Cyclosilanes.

A wide variety of cyclosilanes have been prepared by reductive coupling of the respective dichlorosilanes as has been discussed in several reviews[1,2]. The thermodynamically preferred ring size is dependent on the size of substituents. For alkyl substituents, the ring size varies widely depending on the length of the alkyl chains. For example, with dimethyl substituted silicon atoms, the cyclohexasilane is thermodynamically favored[19] whereas with dihexyl substituted silicon atoms the five membered ring is preferred[20], but large proportions of the four membered ring can be formed under kinetically controlled conditions. For HexMeSi the preferred ring size is the five membered ring, but four membered rings are also formed during the reductive coupling process. Replacing the hexyl group with a phenyl group results in the five membered ring being the preferred size with no four membered rings being observed. With diphenyl substitution the preferred ring size is the five membered ring, however, up to 30% of the four membered ring has been reported as a kinetic product[21]. Bulkier mesityl substituents lead to the formation of the cyclotrisilane as the exclusive cyclic product.

Table 1. Thermodynamically preferred ring sizes of variously disubstituted silylenes. Value in parentheses is the minor cylic product observed during the reductive coupling process.

| Substituent	Me_2Si	PhMeSi	R_2Si	Ph_2Si	$t-Bu_2Si$	Mes_2Si
Preferred ring size	6 (5,7)	5(6)	5,4	5 (4)	3 (2)	3 (2)

Both the hexamesitylcyclotrisilane and octaphenylcyclotetrasilane possess sufficient ring strain to be polymerized, but cannot be polymerized due to repulsive interactions between the bulky substituents in the hypothetical linear polymer. However, substitution of some of the phenyl groups in octaphenylcyclotetrasilane with smaller substituents, such as methyl groups, leads to polymerizable cyclotetrasilanes in which the ring strain is preserved, but the repulsive interactions upon ring opening are decreased. Removal of mesityl groups was accompanied by ring cleavage and therefore, no polymerizable cyclotrisilanes were obtained. Recently, work in our group has focused on the synthesis of a variety of cyclotetrasilanes with methyl and phenyl substituents, $Me_nPh_{8-n}Si_4$, where n = 3, 4, 5, and 6.

4 ROP OF CYCLOTETRASILANES

4.1 Synthesis of Monomers

The cyclotetrasilanes were prepared by the route shown in Scheme 2. Treatment of octaphenylcyclotetrasilane with up to four equivalents of trifluormethanesulfonic acid resulted in the corresponding trifluoromethanesulfonate, or triflate, intermediates by a dearylation reaction. When more than four equivalents of acid were used ring cleavage

competed with substitution[22]. Subsequent reaction of the triflate intermediates with methylmagnesium bromide resulted in the desired methyl and phenyl substituted cyclosilanes. Penta- and hexamethyl substituted rings were afforded by the treatment of $Me_4Ph_4Si_4$ with one or two equivalents of triflic acid followed by methylation[12].
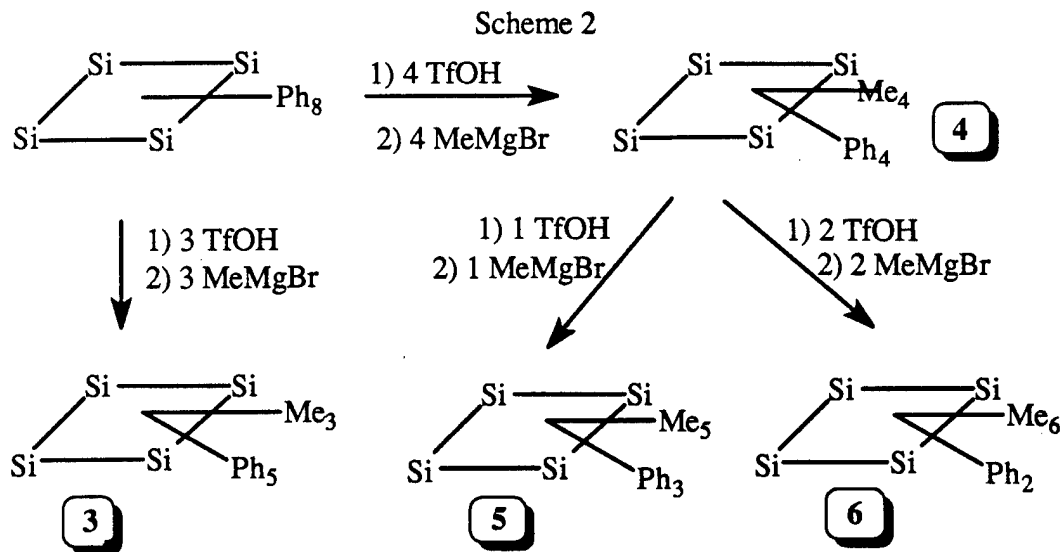
Scheme 2

The synthesis of $Me_4Ph_4Si_4$ results in a mixture of three different stereoisomers **4a**, **4b**, and **4c** (Scheme 3). The dominant isomer in the synthesis has been shown to possess an all-trans configuration of substituents and can be enriched to 95% by recrystallization in cold hexane[12]. The other two isomers have been identified as well, but have not been isolated.

Scheme 3
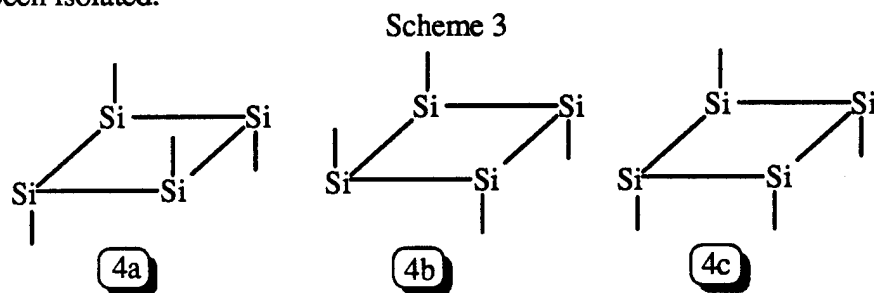
The enthalpy of polymerization in **4** was estimated by differential scanning calorimetry (DSC). $Me_4Ph_4Si_4$ has been found to polymerize spontaneously upon heating to 150 °C. A representative DSC trace for a sample of this monomer is shown in Figure 1. The trace shows two thermal transitions, the first being an endothermic transition beginning near 90 °C which is ascribe to a melting transition for some of the isomers. The second transition is a large exotherm with an onset temperature of 145 °C which is assigned to the heat released during the ROP process. The enthalpy of polymerization for $Me_4Ph_4Si_4$ has been determined to be -56 kJ/mol.

However, when ethyl groups where used instead of the methyl substituents, the formed $Et_4Ph_4Si_4$ was found to be ionically non-polymerizable. Several other cyclotetrasilanes where prepared by the chemical modification method including $(CH_3C≡C)_4Ph_4Si_4$, $(CH_3O)_8Si_4$, and $(CN)_4Ph_4Si_4$ and were successfully polymerized. Two other cyclotetrasilanes have been polymerized thermally by Worsfold. $Me_4Hex_4Si_4$ and $Me_4Pr_4Si_4$ were prepared by the reductive coupling of the respective dichlorosilanes

and were found to undergo thermal polymerization above 100 °C to yield the corresponding linear polysilylenes[23].
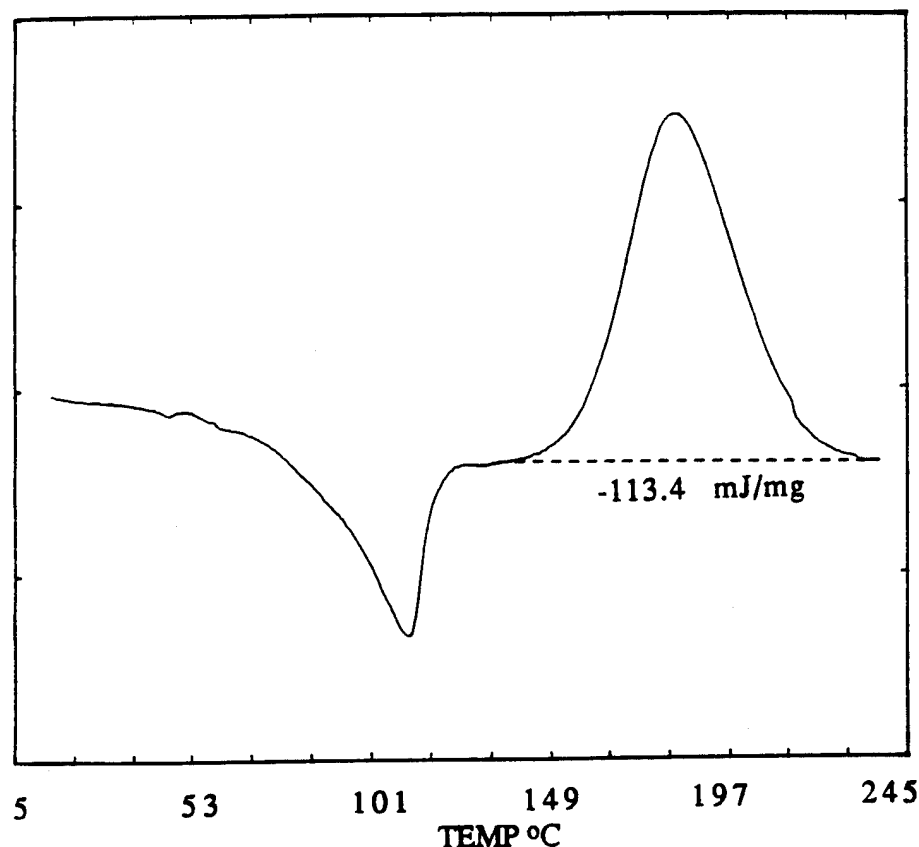

Figure 1. *Differential Scanning Calorimetry trace of 4 in a heating scan from 0 °C to 250 °C in a sealed pan.*

## 4.2 Polymerization of Cyclosilanes.

To prepare linear polysilylenes in a clean fashion the method of polymerization must meet several constraints. First, the only bonds which may be cleaved are Si-Si bonds otherwise defects will be present in the resulting polymer which may affect the electronic properties. Depending on the nature of the other bonds present in the monomer, Si-C and C-H, side reactions may result in new active species too unreactive to reinitate polymerization. This would lead to termination of polymerization and result in low yields of polymer. Even if the newly formed active species are reactive enough to reinitiate polymerization, broad molecular weight distributions may result. Therefore, side reactions should be suppressed for the efficient conversion of cyclosilanes to linear polymers.

Second, the cleavage of Si-Si bonds must be selective to the ring bonds and not bonds present in the linear chain. Enthalpic factors favor the ring opening process however, entropic factors favor intramolecular Si-Si bond cleavage leading to cyclic compounds. A general route for the anionic ROP of $Me_4Ph_4Si_4$ is shown in Scheme 4. Cleavage of Si-Si bonds present in the linear chain may occur by a backbiting process leading to the thermodynamically more stable five and six membered rings. This backbiting process must be eliminated for a successful ROP of cyclotetrasilanes to be carried out. Polymerization of $Me_4Ph_4Si_4$ using n-BuLi/[2.1.1] cryptand in benzene leads

to high yields of polymer as long as the reaction is terminated before the backbiting process can compete (1 h, backbiting begins after 3 h, depending on $[I]_0$).

The molecular weights in the n-BuLi initiated polymerization were not controlled by ratio of concentrations of the monomer to initiator and polydispersities were $M_w/M_n > 2$.

Scheme 4
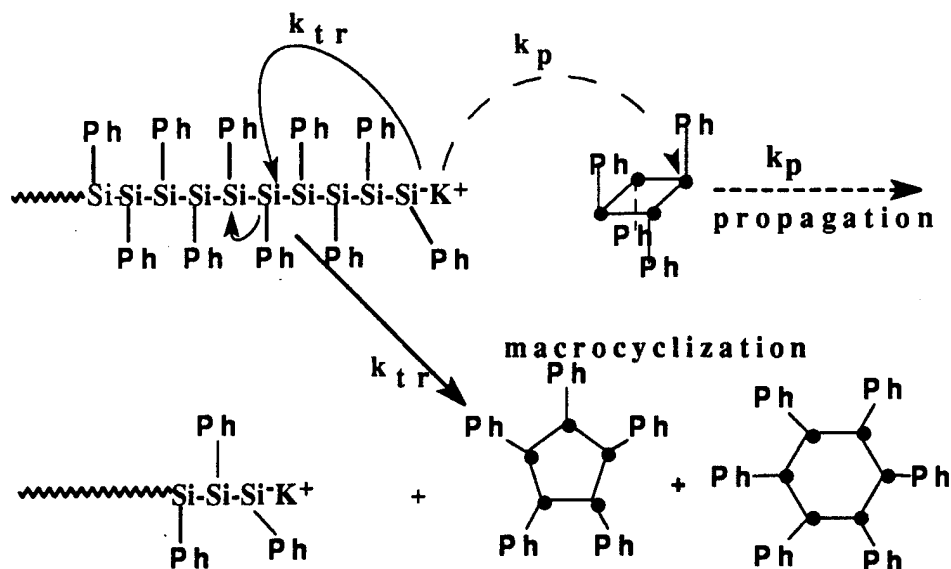
This results from several different factors which may play a role in the polymerization. If the initiator efficiency is low, molecular weights will be higher than expected from $[M]_0/[I]_0$. The simultaneous presence of different types of active centers, such as free ions, ion pairs, or covalent metal-silicon bonds, and potential aggregation may give rise to significantly different reactivities resulting in the observed polymerization behavior. In order to attain a higher degree of control in the ROP of cyclotetrasilanes more selective systems were explored. A variety of transition metal based initiators were studied with silyl cuprates, $(R_3Si)_nCu(CN)Li_n$, giving rise to the best results in regard to molecular weight control and molecular weight distributions.

4.3 Stereochemistry.

One of the most promising advantages of the ROP of cyclotetrasilanes is the potential for control of the resulting microstructure. Polymerization of the all-trans isomer, 4a, can result in several different microstructures depending on the mechanism of ROP. The possibilities are shown in Scheme 5. If the polymerization occurs with two inversions of configuration at both the attacked silicon atom in the ring and the newly formed reactive center a heterotactic tetrad, mrm, will be built up, where m = a meso juncture and r = a racemic juncture. It should be noted that attack of a propagating chain may occur at either of two prochiral faces of each silicon atom in the ring. This leads to junctures between tetrads which may be either meso or racemic. The net effect is a sequence of [(mrm)m/r] or a polymer with 75% heterotactic triads, 0% syndiotactic triads, and 25% isotactic triads.

If ROP proceeds with two retentions of configuration, a syndiotactic, rrr, tetrad results. If the two possibilities for junctures, m/r, are considered, a sequence of [(rrr)m/r] is built up corresponding to 75% syndiotactic, 0% isotactic, and 25% heterotactic triads. If ROP occurs with a combination of retentions and inversions of configuration, a sequence of [(rrm)m/r] would result, corresponding to a polymer with 50% heterotactic, 37.5% isotactic, and 12.5% syndiotactic triads.

The microstructures of polymers obtained from ROP of different mixtures of the stereoisomers can be calculated as the additive function of all of the components. The predicted microstructures resulting from ROP of a mixture of stereoisomers consisting of 28% of 4a, 14% of 4b, 58% of 4c are shown in Table 2. By comparison of the ^{29}Si

NMR spectra of polymerizations of **4a** with those from mixtures of the isomers it was possible to assign the resulting microstructures and determine the polymerization mechanisms with the different systems.

Scheme 5.

$k_B = k_A$

2X Ret.	2X Inv.	Inv. & Ret.
$[(rrr)r/m]_n$	$[(mrm)m/r]_n$	$[(mrr)m/r]n$
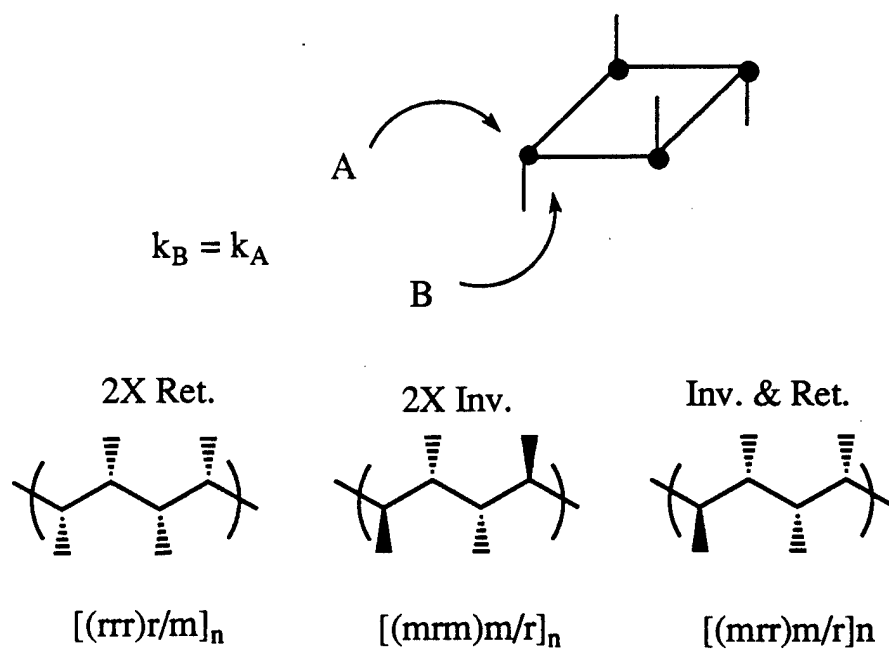
	2 X RET	2 X INV	INV & RET
% hetero (mr=rm)	25	75	50
% syndio (rr)	75	-	37.5
% iso (mm)	-	25	12.5

TABLE 2   Expected and observed tacticities for the silyl cuprate, $(PhMe_2Si)_2Cu(CN)Li_2$ initiated polymerization of a mixture of stereoisomers (28% **4a**, 14% **4b**, 58% **4c**).

Route	% hetero	% syndio	% iso
2 X RET	46.5	37.25	16.25
2 X INV	53.5	19.75	26.75
Obs. mixt.	58.0	15.0	27.0

Figure 2 contains ^{29}Si NMR spectra of poly(methylphenylsilylene) prepared by the reductive coupling of methylphenyldichlorosilane, ROP of $Me_4Ph_4Si_4$ initiated by n-BuLi/[2.1.1]/cryptand, and by the silyl cuprate initiated ROP of the all-trans isomer and a mixture of isomers, respectively. Previous reports have assigned the three peaks in

spectrum 2a to isotactic (-38.5 ppm), syndiotactic (-39.0 ppm), and heterotactic (-41.0 ppm) triads[24]. However, by comparison of spectrum 2c and 2d (and Table 2) it is apparent that the assignments should be heterotactic, syndiotactic, and isotactic, respectively.
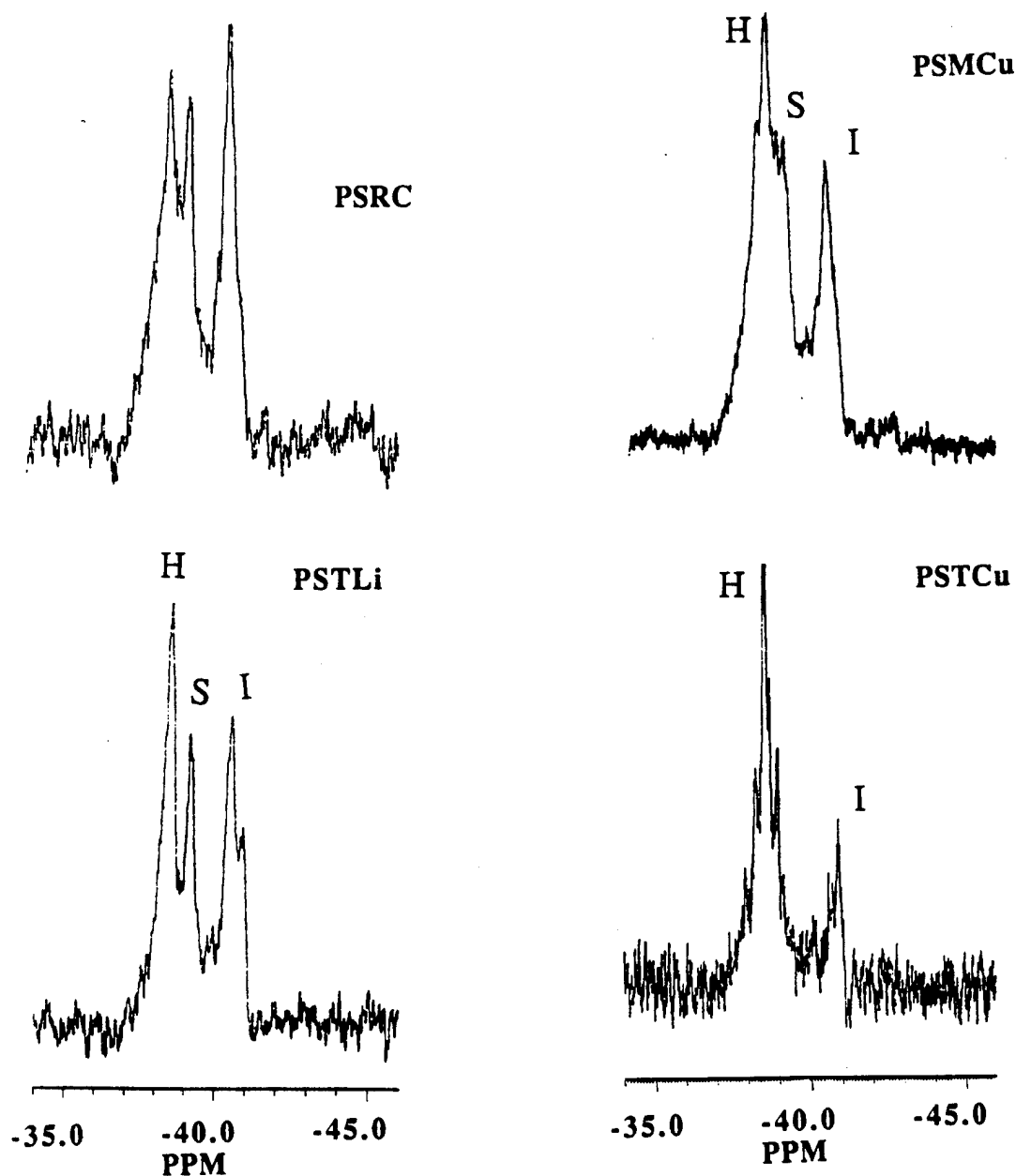

Figure 2. ^{29}Si NMR spectra of PMPS prepared by a) (PSRC) the reductive coupling of PhMeSiCl2, b) (PSTLi) n-BuLi initiated polymerization of 4a, c) (PSTCu) silyl cuprate initiated polymerization of 4a, and d) (PSMCu) silyl cuprate initiated polymerization of a mixture of isomers.

4.4 Mechanisms of ROP.

From the percentage of the various triads present in the prepared polymers tentative mechanisms can be proposed. For the polymerization initiated by

$(PhMe_2Si)_2Cu(CN)Li_2$ it is apparent that the polymerization occurs with *two inversions* of configuration at both the attacked silicon atom in the ring and the newly formed reactive center. Propagation may involve the formation of a pentacoordinated intermediate followed by rapid ring opening. First order kinetics were observed for the cuprate polymerizations of **4a** and indicate that formation of the pentacoordinate intermediate is rate determining. There are two long apical bonds and three shorter equatorial bonds present in pentacoordinated silicon atoms.

Only the weak apical bonds can be cleaved and the bulkiest substituents are preferentially located in apical positions. Strained rings, such as cyclotetrasilanes cannot be positioned with two bonds in equatorial positions which requires that one of the bonds must be present in an apical position. All of the available information on the chemistry of pentacoordinated silicon atoms and on the pseudorotation process leads to the conclusion that the bulky polymer chain and one of the bonds from the monomer must be in apical positions[25,26]. This results in an inversion of the configuration at the attacked Si atom during nucleophilic ROP. The inversion at the second Si atom, which becomes a new growing center, may be due to the bulky nature of the silylcuprate species, or its aggregated nature.

<div align="center">Scheme 6</div>
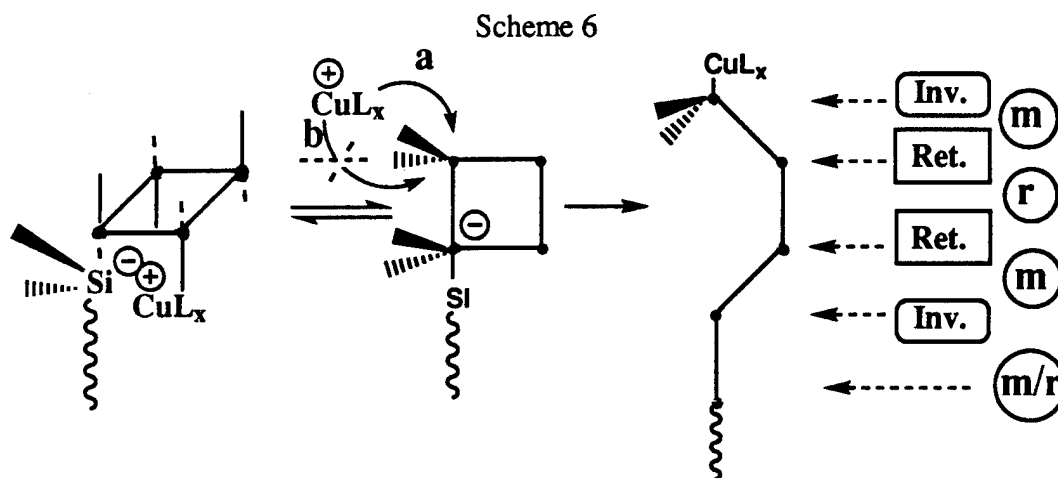
ROP with n-BuLi/[2.1.1] cryptand gave rise to PMPS with a microstructure consisting of 50% heterotactic, 15% syndiotactic, and 35% isotactic triads. This observation leads to a proposed mechanism in which there is an inversion of configuration at the attacked silicon atom and incomplete racemization at the newly formed reactive center. Racemization at the newly formed reactive center most likely occurs because with cryptated Li$^+$ as the counterion the silicon anion can undergo pyramidal inversion more easily than with the bulky cuprate.

4.5 Regiochemistry in the ROP of $Me_3Ph_5Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$.

In the non-symmetrically substituted cyclotetrasilanes it is also possible to explore the regioselectivity of ROP. Analysis of the microstructure of polymers prepared by the ROP of $Me_3Ph_5Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$ allows for the direct observation of steric and stabilization effects of Ph_2Si, $PhMeSi$, and Me_2Si units. The relative stability of formed anions follows the order $Ph_2Si > PhMeSi > Me_2Si$, while the steric hindrance to attack at a silicon atom in the ring should follow the opposite trend.

Polymerizations were carried out using silyl cuprates as initiators under conditions identical to those used for $Me_4Ph_4Si_4$ yielding poly **3** ($Me_3Ph_5Si_4$), poly **5** ($Me_5Ph_3Si_4$), and poly **6** ($Me_6Ph_2Si_4$). The regiochemistry was determined by ^{29}Si NMR studies and by comparison to spectra for PMPS. The ^{29}Si NMR spectra are shown in Figure 3 along with the spectrum from PMPS prepared by the silyl cuprate polymerization of $Me_4Ph_4Si_4$.

For poly **3** two broad peaks are present centered at -30.5 and -38.5 ppm. The peak at -30.5 ppm is assigned to the Ph$_2$Si units and the peak at -38.5 ppm to PhMeSi units. The absence of the isotactic peak for PMPS at -41.0 ppm indicates that ROP occurs with some degree of selectivity, otherwise longer segments of PhMeSi units would be present and some isotactic triads could be formed. However, the broadness of the peak for Ph$_2$Si units indicates that many different environments exist in the polymer, both configurational and conformational.
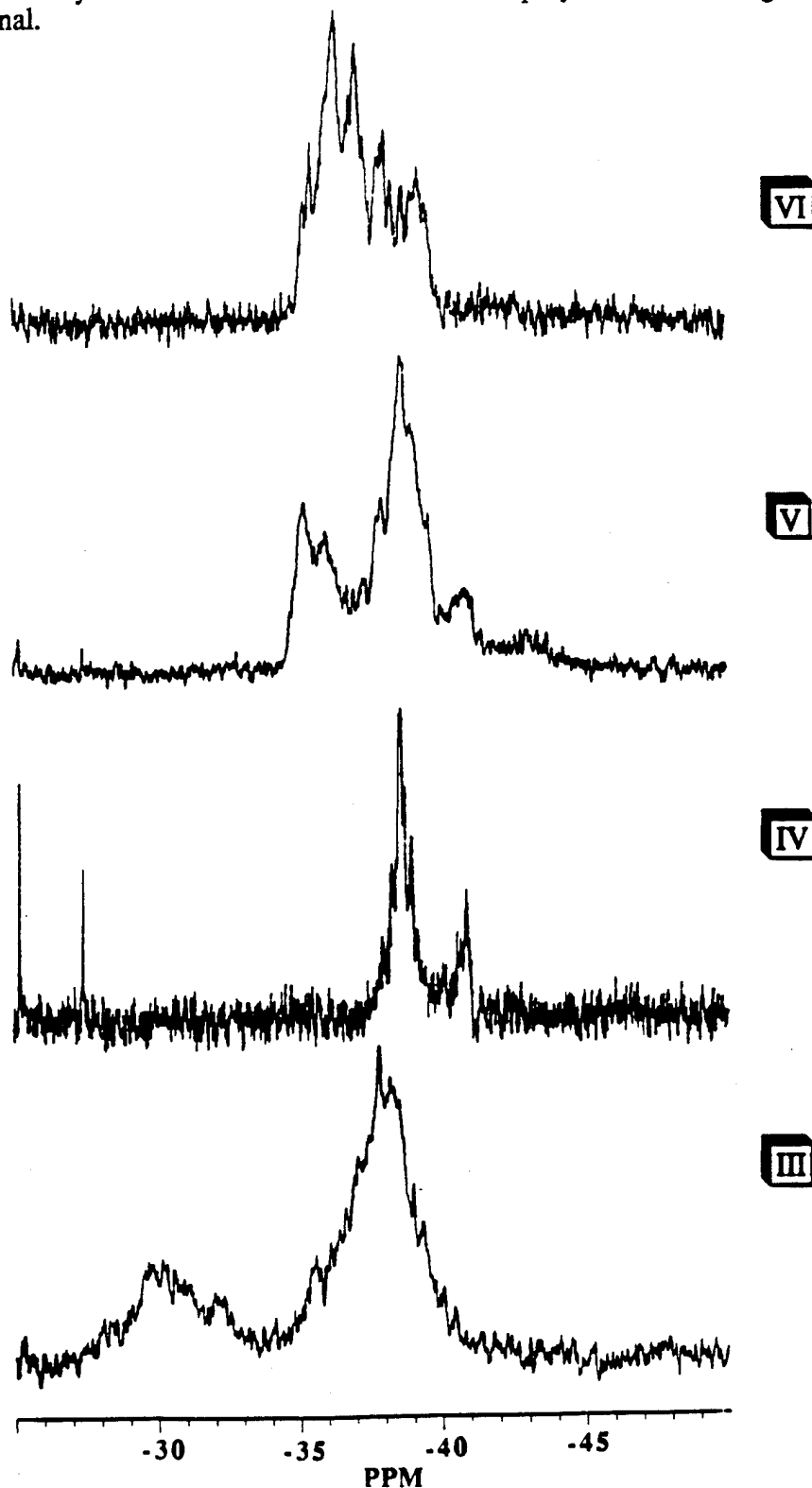

Figure 3. ^{29}Si NMR spectra of poly 3,4,5, and 6.

For poly **5** three broad resonances are observed at -36.5, -39.0, and -41.0 ppm which are assigned to Me_2Si and the latter two to $PhMeSi$ units, respectively. In **5** the $MePhSi$ units are arranged so that the methyl groups are trans to each other. If the same mechanism of polymerization as was observed for **4** is assumed a series of heterotactic triads will be seen, but separated by Me_2Si unit spacers. The presence of a small resonance at -41.0 ppm indicates that polymerization occurs with incomplete regioselectivity. The Me_2Si region contains two individual resonances which may result from the two ways in which the heterotactic triads of $MePhSi$ units may be coupled to Me_2Si units.

The ROP of $Me_6Ph_2Si_4$ was carried out on a mixture of geometrical (1,1,2,2,3,4-hexamethyl and 1,1,2,3,3,4-hexamethyl) isomers which makes determination of the precise regiochemistry impossible. However, the absence of any heterotactic triads indicates some selectively in the attack of a $PhMeSi$ anion on a Me_2Si unit in the ring.

The electronic properties of the resulting polymers were studied by UV and fluorescence spectroscopy. The observed λ_{max} in all polymers correlated with the percentage of phenyl substituents in the starting monomer. Relevant data are given in Table 3. It should be noted that copolymers of this type prepared by the reductive coupling of a mixture of dichlorosilanes are blocky in nature and the ROP prohibits the formation of long segments of individual components to be formed.

Table 3. Molecular weight, absorbance, and emission data for polymers prepared by the silyl cuprate polymerization of $Me_3Ph_5Si_4$, $Me_4Ph_4Si_4$, $Me_5Ph_3Si_4$, and $Me_6Ph_2Si_4$.

Polymer	$\overline{M_n}$	$\overline{M_w/M_n}$	Absorbance λ_{max} (nm)	Emission λ_{max} (nm)
$Me_3Ph_5Si_4$ **3**	25,000	1.5	353	376
$Me_4Ph_4Si_4$ **4**	36,000	1.6	338	365
$Me_5Ph_2Si_4$ **5**	10,500	2.0	332	360
$Me_6Ph_2Si_4$ **6**	12,000	1.6	328	355

5 SYNTHETIC POSSIBILITIES

Because the ROP is a versatile method for preparing polysilylenes with well-defined structures it becomes possible to utilize the system to prepare materials which cannot be prepared by other methods. For example, the preparation of block copolymers of polysilylenes with other polymers has been elusive, except in the case of masked disilene polymerizations and the coupling reaction of polystyryl lithium with halide capped polysilylenes[10,27]. Block copolymers have also been prepared by using polysilylenes to photoinitiate the radical polymerization of vinyl monomers[28]. Using the anionic polymerization of cyclotetrasilanes in conjunction with the living polymerizations of styrene and isoprene it has been possible to prepare well-defined block copolymers.

5.1 Polystyrene-block-PMPS and Polyisoprene-block-PMPS

Polystyrene-block-PMPS and polyisoprene-block-PMPS were prepared by initiating the ROP of $Me_4Ph_4Si_4$ with polystyryl lithium and polyisoprenyl lithium, respectively. A stoichiometric amount of 12-crown-4, based on lithium, was required to initiate polymerization. Polymerizations were followed by size exclusion chromatography (SEC). Significant increases in molecular weight were observed after addition of the

cyclotetrasilane to either the polystyryl lithium or polyisoprenyl lithium solutions. Relevant molecular weight data are given in Table 4.

Table 4. Molecular weight data for homo polystyrene and polyisoprene and block copolymers with poly(methylphenylsilylene) prepared by the subsequent addition of **4** to polystyryl lithium and polyisoprenyl lithium, respectively.

(polystyrene)

$[St]_o$	$[I]_o$	DP_t^1/DP_e^1	M_w/M_n	$[Si_4]_o$	$[I]_o$	$M_{n(total)}$	M_w/M_n	DP_t^2/DP_e^2
0.91	0.04	23/23	1.16	0.23	0.015	13,900	1.34	15/24 (18)[a]
1.80	0.04	46/51	1.15	0.23	0.015	16,300	1.31	15/23 (20)[a]

(polyisoprene)

$[Iso]_o$	$[I]_o$	DP_t^1/DP_e^1	M_w/M_n	$[Si_4]_o$	$[I]_o$	$M_{n(total)}$	M_w/M_n	DP_t^2/DP_e^2
2.2	0.036	61/54	1.13	0.342	0.015	13,360	1.32	21/20 (24)[a]
2.0	0.073	27/22	1.11	0.350	0.030	5,600	1.40	12/9 (9)[a]

a) determined by integration of ^1H NMR spectra.
b) concentrations are expressed in mol/L.

In all experiments with polystyrene the molecular weights observed for the PMPS blocks were nearly double that of the expected value while the values for the polyisoprene copolymers are similar to the expected values. By comparison with molecular weights detemined by integration of the ^1H NMR spectra of the copolymers it was possible to determine a more accurate value for the PMPS segments. The values for the polystyrene blocks are intermediate between the expected values and those determined by SEC and indicate an initiator efficiency of near 70% for the ROP. The SEC values may be somewhat high because the block copolymer may not form a true random coil in solution.

5.2 Cyclotetrasilane/Masked Disilene Copolymerizations.

Preparation of the first block copolymer of two different polysilylenes was achieved by combining the ROP of cyclotetrasilanes with the anionic polymerization of masked disilenes . Attempts to prepare block copolymers by subsequent addition of monomers lead to mixtures of products including both homopolymers and some block copolymer. Whereas, simultaneous copolymerization of the two monomers in THF solution resulted in the desired product. The polymerization procedure involved dissolving the masked disilene and cyclotetrasilane in THF and lowering the temperature to -40 °C (the masked disilene does not polymerize at this temperature) at which time the initiator (n-BuLi) was added. Polymerization of the masked disilene was afforded by warming the mixture to room temperature before termination.

The polymers were soluble in hexane whereas PMPS is not, indicating formation of block copolymers. The copolymers were studied by ^{29}Si NMR spectroscopy which resulted in spectra which contained resonances identical to those found for both homopolymers and some additional peaks for cross-over points (Figure 4). The electronic properties of the copolymers appears to be a composite of the two individual components and thus, the UV spectra are similar to mixtures of the two homopolymers.
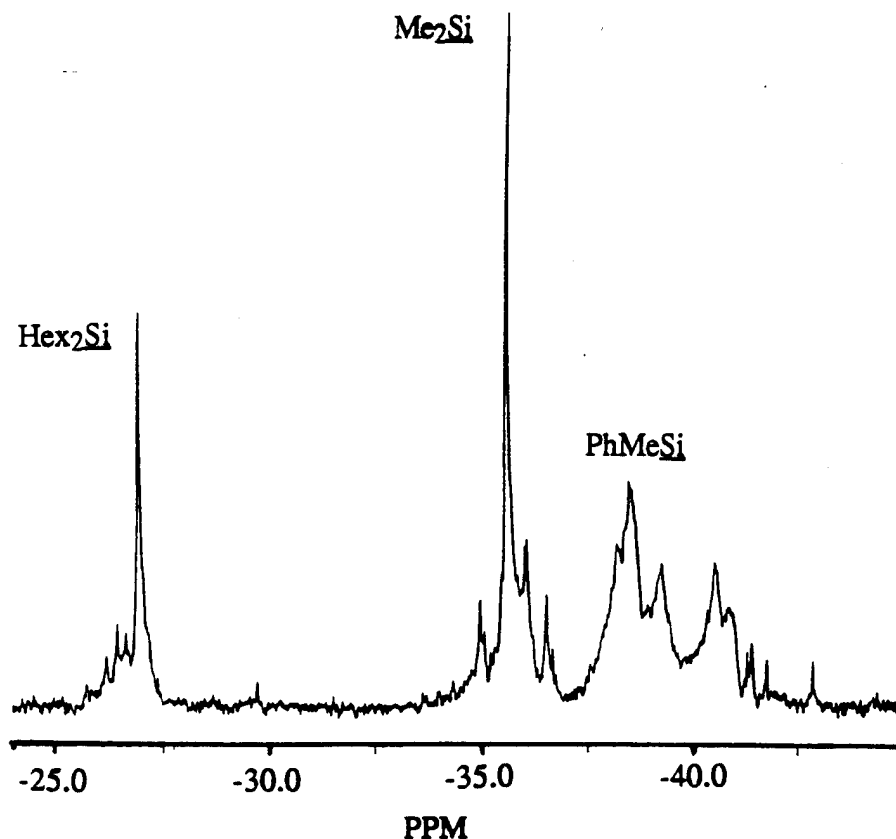
Figure 4. ^{29}Si NMR spectrum of the copolymer formed by simultaneous copolymerization of a masked disilene and 4 in THF.

5.3 Poly(ferrocenylsilane)/PMPS copolymers.

Much interest has been devoted in recent years to the incorporation of transition metals into the backbone and as pendant groups in polymers. Recent reports have described the thermal ring opening polymerization of [1]-silylferrocenophanes to form high molecular weight, linear polymers[29]. Thermal copolymerizations of cyclotetrasilanes and [1]-silylferrocenophanes were investigated in order to prepare copolymers.

From the previously described thermodynamic studies of cyclotetrasilanes a polymerization onset temperature of 150 °C was determined, thus thermal copolymerizations and homopolymerizations were carried out in sealed tubes at 150 °C for 2 hours. ^1H NMR analysis indicated quantitative conversions to polymer (no monomers were detected). Molecular weights determined by Size Exclusion Chromatography are given in Table 5.

Table 5 Thermal Copolymerization Experiments involving $Me_4Ph_4Si_4$ and $FcSiMe_2$.
a) after photodegradation, b) determined by DSC

Si_4:$FcSiMe_2$	M_n (PDI)	M_n (PDI)[a]	λ_{max} (nm)	$T_g(^oC)$[b]
mol:mol	---	---	---	---
0:1	250,000(1.6)	230,000(1.9)	---	33
1:2.2	89,000(3.5)	1,730(1.4)	325	69
1:1	75,000(3.1)	1,410(1.2)	330	---
2:1	67,000(2.4)	1,050(1.4)	333	---
1:0	91,000(3.0)	---	338	---

The molecular weight distributions, M_w/M_n, for copolymers are higher than for the homo poly(ferrocenylsilane). Evidence for the formation of true copolymers was achieved by photodegradation of the PMPS segments which left the poly(ferrocenylsilane) segments intact. By following the SEC traces at different wavelengths unique to the individual components it was possible to prove the existence of copolymers. Representative traces are shown in Figure 5. Before degradation, the two traces at 330 nm (unique to PMPS) and 450 nm (unique to ferrocene) overlapped exactly.
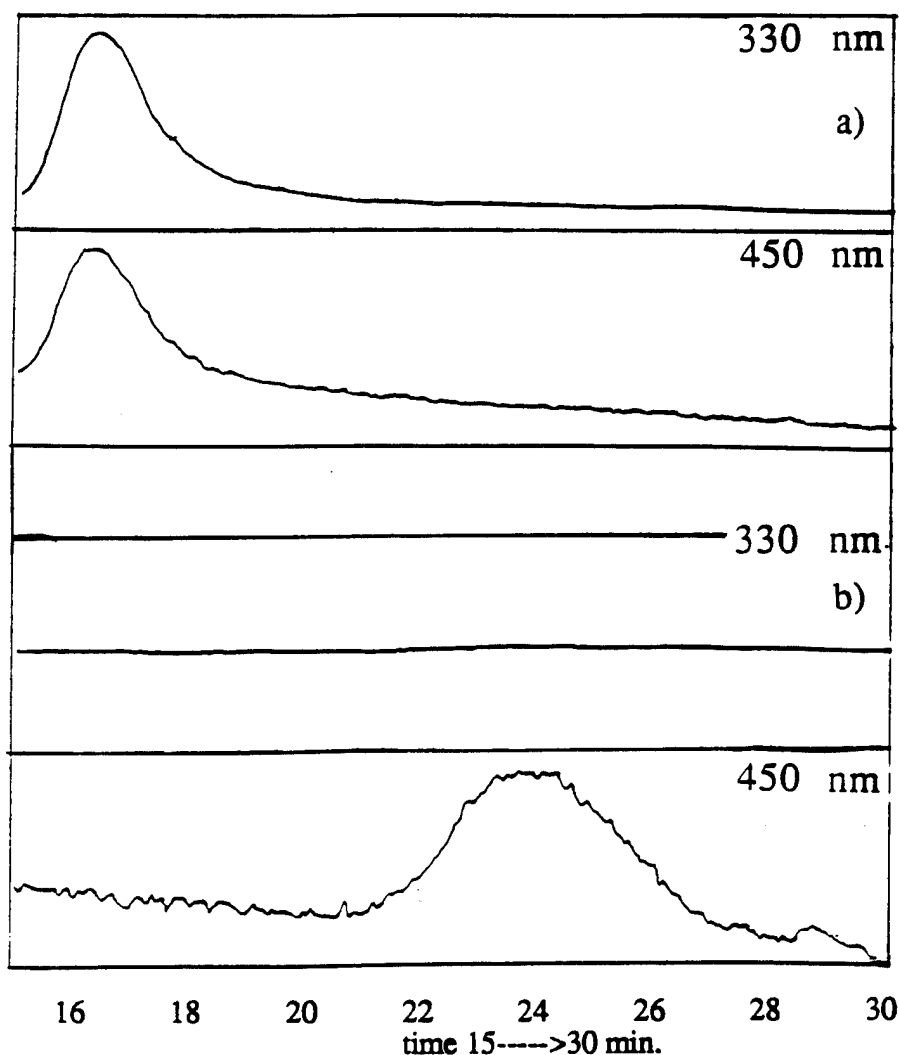

Figure 5. *SEC traces for copolymers prepared by the thermal copolymerization of 4 and [1]-dimethylsilylferrocenophane at 330 and 450 nm a) before degradation and b) photodegraded sample.*

After photodegradation, the signal at 330 nm was absent and the trace at 450 nm was shifted to considerably lower molecular weights. This lead to the conclusion that copolymers were indeed formed and consisted of short segments of each individual component.

The segment length of individual components appears to correlate with the percentage of the respective monomer in the starting mixture (Table 5). The length of the poly(ferrocenylsilane) segments varied from 2 to 10 repeat units. The λ_{max} for the PMPS

segments showed an increase with a higher percentage of the cyclotetrasilane which indicated that the PMPS segments were increasing in length until the ultimate maximum of 338 nm was reached[30].

CONCLUSIONS

The ROP of cyclotetrasilanes is an interesting and versatile method to prepare both polysilylenes homo and copolymers which cannot be prepared by other methods. A variety of cyclotetrasilanes, $Me_nPh_{8-n}Si_4$, where n = 3, 4, 5, or 6, were prepared and polymerized using silyl cuprates as initiators. The polymerization of the all-trans isomer of $Me_4Ph_4Si_4$ proceeds with two inversions of configuration at both the attacked silicon atom in the ring and the newly formed reactive center resulting in a polymer with 75% heterotactic triads and 25% isotactic triads. Polymerization of the tri-, penta-, and hexamethyl derivatives proceeds with some degree of regioselectivity. Block copolymers were prepared by the subsequent addition of $Me_4Ph_4Si_4$ to either polystyryl lithium or polyisoprenyl lithium. A novel block copolymer of two different polysilylenes was prepared by the copolymerization of a masked disilene and $Me_4Ph_4Si_4$. Segmental copolymers of poly(ferrocenylsilane) and PMPS were prepared by the thermal copolymerization of $Me_4Ph_4Si_4$ and [1]-silylferrocenophanes.

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References.

1. J. Michl; R. D. Miller *Chem. Rev.* 1989, **89**, 1359.
2. R. West *J. Organomet. Chem.* 1986, **300**, 327.
3. K. Matyjaszewski; M. Cypryk; H. Frey; J. Hrkach; H. K. Kim; M. Moeller; K. Ruehl; M. White *J. Macromol. Sci., Chem.* 1991, **A28**, 1151.
4. W. E. Rochefort; G. W. Heffner; D. S. Pearson; R. D. Miller; P. M. Cotts *Macromolecules* 1991, **24**, 4861.
5. W. J. Welsh; J. R. D. Jr.; R. C. West *Macromolecules* 1989, **22**, 2947.
6. P. R. Sundararajan *Macromolecules* 1988, **21**, 1256.
7. R. D. Miller; B. L. Farmer; W. W. Fleming; R. Sooriyakumaran; J. F. Rabolt *J. Am. Chem. Soc.* 1987, **109**, 2509.
8. F. C. Schilling; A. J. Lovinger; D. D. Davis; F. A. Bovey; J. M. Zeigler *Macromolecules* 1989, **22**, 3055.
9. T. D. Tilley *Acc. Chem. Res.* 1993, **26**, 22.
10. K. Sakamoto; K. Obata; H. Hirata; M. Nakajima; H. Sakurai *J. Am. Chem. Soc.* 1989, **111**, 7641.
11. M. Cypryk; Y. Gupta; K. Matyjaszewski *J. Am. Chem. Soc.* 1991, **113**, 1046.
12. E. Fossum; S. W. Gordon-Wylie; K. Matyjaszewski *Organometallics* 1994, **13**, 1695.
13. K. Matyjaszewski *Makromol. Chem. Macromol. Symp.* 1991, **42/43**, 269.
14. E. Fossum; K. Matyjaszewski *American Chemical Society Polymer Preprints* 1994, **35**.
15. M. Suzuki; J. Kotani; S. Gyobu; T. Kaneko; T. Saegusa *Macromolecules* 1994, **27**, 2360.
16. S. Penczek; K. Matyjaszewski *J. Polym. Sci. Symp.* 1976, **56**, 255.
17. T. Tsumuraya; S. A. Batcheller; S. Masamune *Angew. Chem. Int. Ed. Eng.* 1991, **30**, 902.
18. R. West; M. J. Fink; J. Michl *Science* 1981, **214**, 1343.
19. L. F. Brough; R. West *J. Organomet. Chem.* 1980, **194**, 139.

20. H. K. Kim; K. Matyjaszewski *J. Polymer Science, Part A. Polym. Chem.* 1993, **31**, 299.

21. H. Gilman; G. L. Schwebke *J. Organomet. Chem.* 1965, **3**, 382.

22. J. Chrusciel; M. Cypryk; E. Fossum; K. Matyjaszewski *Organometallics* 1992, **11**, 3257.

23. S. Gauthier; D. J. Worsfold *Inorganic and Organometallic Oligomers and Polymers* 1991, J. F. Harrod and R. M. Laine, Eds., 37.

24. J. Maxka; F. K. Mitter; D. R. Powell; R. West *Organometallics* 1991, **10**, 660.

25. R. J. P. Corriu; J. C. Young *The Silicon Heteratom Bond* 1991, S. Patai and A. Rappoport, Eds., 1.

26. R. P. Holmes *Chem. Rev.* 1990, **90**, 17.

27. S. Demouster-Champagne; A.-F. de Mahieu; J. Devaux; R. Fayt; P. J. Teyssie *J. Polym. Sci. Polym. Chem.* 1993, **33**, 2009.

28. R. West; A. Wolff; D. J. Peterson *J. Rad. Curing* 1986, 35.

29. D. A. Foucher; B. Z. Tang; I. Manners *J. Am. Chem. Soc.* 1992, **114**, 6246.

30. C. Strazielle; A. F. De Mahieu; D. Daoust; J. Devaux *Polymer* 1992, **33**, 4174.